

T-12

## Theoretical Chemistry &amp; Molecular Physics

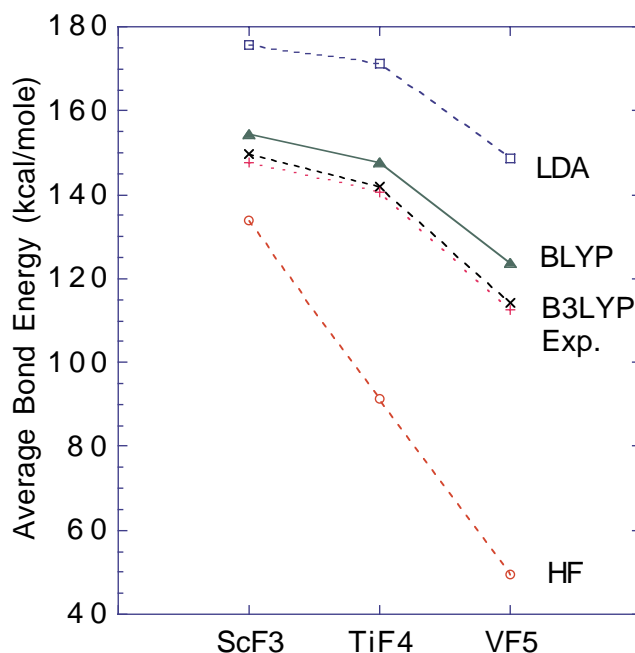
**Hybrid Density Functional Theory**

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Density functional theory<sup>1</sup> is based on the theorem of Hohenberg and Kohn which states that the total energy of a many-body system is a functional of the electron density only. Kohn and Sham formulated a practical implementation by introducing a fictitious single determinant of one electron orbitals whose density is identical to that of the fully interacting system, and whose energy may be computed as the sum of the kinetic energy, classical Coulomb repulsion and external potential terms, and an “exchange-correlation” energy. The beauty of this approach is that the total energy of the fully-interacting system may be extracted from the single determinant of fictitious orbitals, given the “exchange-correlation” functional.

The functional itself is not specified by the theory. It was first assumed that the functional could be approximated by the density locally, and since the functional is universal, a form extracted from essentially-exact electron gas solutions became the de facto standard in solid state physics. This local density approximation (LDA) has been extremely successful in describing the properties of many condensed matter systems. It generally gives reliable structural predictions, electron band dispersions, and phonon frequencies. As useful as it has been, there are shortcomings as well. Among these are a tendency to overestimate the cohesive energy and to predict

metallic behavior in the case of narrow band or nearly localized electrons. An example of the latter is the LDA prediction that the parent compound of the high-temperature superconductors,  $\text{La}_2\text{CuO}_4$ , should be a metal, when in fact it is an antiferromagnetic insulator with a gap of about 2 eV.



**Figure 1: The average bond energies in a series of transition-metal fluorides as computed in various approximations. These include Hartree-Fock (HF), the local density approximation (LDA), a gradient-corrected approximation (BLYP), and a hybrid method (B3LYP).**

~ 30 kcal/mole. In the past few years, the LDA has been improved through the development of functionals which depend on the local density and its gradient invariants, thereby including some nonlocal character. Figure 1 shows that a gradient-corrected functional (BLYP) is a marked improvement, yielding errors of only ~ 10 kcal/mole in the average bond energies of the metal-fluorides.

It is the overestimation of the cohesive energy, however, that has delayed the acceptance of density functional theory in the quantum chemistry community. Chemistry is about making and breaking bonds, and the energy of a reaction in which one bond is broken and another formed can be of the order of a few kcal/mole, whereas the error in the LDA bond energy can easily be as large as 30 kcal/mole. An example is found in Figure 1, where the average metal-fluorine bond energy in a series of transition metal fluorides as computed by the LDA is compared to experiment.<sup>2</sup> It rather consistently overestimates the average bond energy by

Becke<sup>3</sup> has argued that improved functionals may be generated by consideration of the adiabatic connection formula. The price paid for simplifying the energy expression through the introduction of a fictitious noninteracting system is that the exchange-correlation energy is given by an integral

$$E_{xc} = \int_0^1 d\lambda U_{xc, \lambda} \quad (1)$$

where  $\lambda$  is a coupling-strength parameter which turns on the Coulomb repulsion between electrons, and  $U_{xc, \lambda}$  is the potential energy of exchange-correlation at coupling strength  $\lambda$ . This formula connects the noninteracting ( $\lambda = 0$ ) system with the fully interacting ( $\lambda = 1$ ) one. It is understood that the density is held constant in this expression at the density of the fully interacting system.

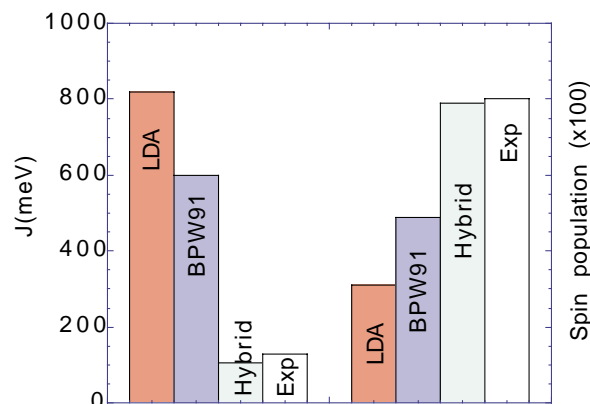
Becke has emphasized that in the  $\lambda = 0$  limit in which there is no correlation, there remains a contribution to the exchange energy  $E_x$  which comes about from the antisymmetry restrictions on the determinant. If the density of the fully interacting system were the Hartree-Fock density, this would simply be the Hartree-Fock exchange energy. He argues that the local density approximation is a particularly poor approximation in this limit, since the “exact” exchange hole is nonlocal, and that it is the unphysical nature of the LDA in this limit which is responsible for its tendency to overbind molecular species. Less is known about the fully interacting limit, but suppose it is fairly well described by the LDA or a gradient-expansion. The simplest two-point approximation to the integral is then

$$E_{xc} = \frac{1}{2}(E_x + U_{xc, \lambda = 1}) \quad (2)$$

There are other hybrids being investigated, but they all merge the LDA or a gradient-corrected functional with the fully nonlocal “exact” exchange interaction. A hybrid functional (B3LYP) similar to the one above, when applied to the metal-fluoride problem, is in remarkable agreement with experiment, as shown in Figure 1. The error in the average bond energy is now of the order of 2 kcal/mole. The theoretical bond lengths are also in excellent agreement with experiment.

We mention one other application of the hybrid functionals<sup>4</sup> which addresses the LDA bias against antiferromagnetism. Table I shows the magnitude of the effective Heisenberg coupling constant ( $J$ ) and the unpaired

spin population ( $P_d$ ) in a cluster model of  $\text{La}_2\text{CuO}_4$  as computed in the LDA, a gradient-corrected approximation (BPW91), and finally a hybrid functional similar to Equation 2. The LDA underestimates the moment, overemphasizing the delocalization or metallic character; the gradient-corrected approximation is a step in the right direction, but the moment is still much too small. The hybrid is in qualitative and semiquantitative agreement with experiment.  $\text{KNiF}_3$  and  $\text{K}_2\text{NiF}_4$  have also been examined with similar success. The magnitude of the coupling constant from the hybrid functional is within  $\sim 20\%$  of experiment in these cases as well.



**Figure 2:** On the left of the figure, the Heisenberg coupling constant computed for  $\text{La}_2\text{CuO}_4$  from the LDA, a gradient-corrected functional (BPW91), and the hybrid functional are compared with experiment. The evolution of the unpaired spin population on the metal site is shown on the right.

While more investigation remains to be done, these methods appear promising in a number of areas. Applications to problems in actinide chemistry, transition metal hydrolysis, and selective oxidation chemistry are in progress.

<sup>1</sup> R. G. Parr and W. Yang, “Density Functional Theory of Atoms and Molecules” (Oxford University Press, New York, 1989).

<sup>2</sup> T. V. Russo, R. L. Martin, and P. J. Hay, *J. Chem. Phys.* **102**, 8023 (1995).

<sup>3</sup> A. D. Becke, *J. Chem. Phys.* **98**, 172 (1993).

<sup>4</sup> R. L. Martin and F. Illas, submitted to *Phys. Rev. Lett.*